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Determination of the trap-assisted recombination strength in polymer light emitting diodes

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The recombination processes in poly(*p*-phenylene vinylene) based polymer light-emitting diodes (PLEDs) are investigated. Photogenerated current measurements on PLED device structures reveal that next to the known Langevin recombination also trap-assisted recombination is an important recombination channel in PLEDs, which has not been considered until now. The dependence of the open-circuit voltage on light intensity enables us to determine the strength of this process. Numerical modeling of the current-voltage characteristics incorporating both Langevin and trap-assisted recombination yields a correct and consistent description of the PLED, without the traditional correction of the Langevin prefactor. At low bias voltage the trap-assisted recombination rate is found to be dominant over the free carrier recombination rate. © *2011 American Institute of Physics*. [doi:10.1063/1.3559911]

In order to increase the efficiency of polymer light-emitting diodes (PLEDs), a fundamental understanding of the charge transport and recombination processes in the polymer is essential. Investigation of the charge transport in PLEDs of poly(*p*-phenylene vinylene) (PPV) derivatives has led to the insight that the charge transport is dominated by holes.[1] The reduced electron transport is attributed to the presence of electrons traps,[2,3] causing the electrons to drift less far into the PLED as compared to the holes. A major disadvantage of this unbalanced carrier transport is that the recombination zone is relatively close to the metallic cathode. As a result, the excitons formed close to the cathode may transfer their energy to the cathode and decay nonradiatively, leading to a loss of efficiency.

It is widely accepted that the recombination mechanism in PLEDs is bimolecular of the Langevin type.[4–7] To what extent the trapped electrons also contribute to the recombination in a PLED is an open question. Earlier research has already given some indications that this contribution might be considerable.[8,9] Modeling done on PPV-based PLEDs has shown that using only Langevin recombination is not entirely sufficient to correctly describe the current-voltage behavior of such a PLED. In order to fit the current density-voltage (J-V) curves the strength of the Langevin recombination needs to be enhanced typically by a factor of 3 or 4.[8,9] This suggests that only taking into account Langevin recombination of free charge carriers is not sufficient and that trap-assisted recombination might play a significant role. A similar observation was made in organic solar cells in which trap-limited electron transport is present. At the open circuit voltage (V_{OC}) there is no current extraction and virtually all photogenerated excitons recombine. As a result, the dependence of the V_{OC} on the light intensity is a sensitive measure for the recombination mechanisms in solar cells.[10–13] The response of the V_{OC} on the light intensity in trap-free solar cells is given by[14]

$$V_{OC} = \frac{E_{gap}}{q} - \frac{kT}{q}\ln\left(\frac{(1-P)BN_{CV}^2}{PG}\right), \tag{1}$$

where P is the dissociation probability of bound electron-hole pairs, E_{gap} is the effective energy gap, N_{cv} is the effective density of states, B is the recombination strength, and G is the generation rate of electron-hole pairs. The generation rate G is proportional to the light intensity in this equation, directly connecting the V_{OC} to the light intensity. Furthermore, for the bimolecular recombination strength the Langevin relation is used[15]

$$B_L = \frac{q}{\varepsilon}(\mu_n + \mu_p), \tag{2}$$

where μ_n and μ_p are the electron and hole mobility, respectively. Equation (1) predicts that the slope of V_{OC} versus the logarithm of the light intensity is equal to the thermal voltage kT/q. It has been demonstrated that this relation holds for solar cells in which both the electron- and hole transport are trap-free, which is the case in most polymer:fullerene bulk heterojunction solar cells.[14] However, if one of the carriers exhibits trap-limited transport, the slope exceeds kT/q. This increase in the dependence of V_{OC} on light intensity can be explained by considering trap-assisted recombination.[10–13] The description for the trap-assisted recombination strength is given by the Shockley–Read–Hall (SRH) equation[16,17]

$$B_{\mathrm{SRH}} = C_n C_p N_t / [C_n(n+n_1) + C_p(p+p_1)], \tag{3}$$

where C_n and C_p are the capture coefficients for electrons and holes, respectively, N_t is the density of electron traps, n and p are the electron density in the conduction band and the hole density in the valence band, respectively, and their product under equilibrium conditions $p_1 n_1 = N_{cv}\exp[-E_{gap}/kT] = n_i^2$, where n_i is the intrinsic carrier concentration in the sample. To obtain the total recombination strength this mechanism is then added to the Langevin relation leading to the expression for V_{OC} to read:

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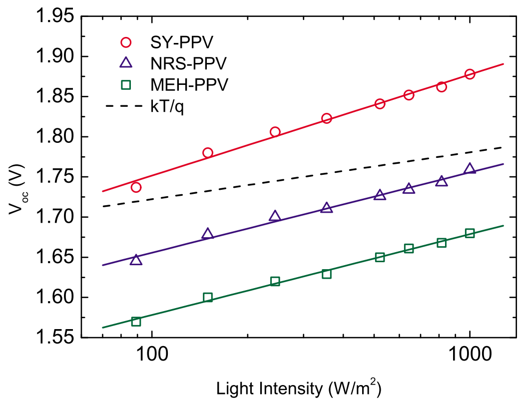

FIG. 1. (Color online) Light intensity dependence of the V_{OC} at room temperature for SY-PPV (120 nm), NRS-PPV (98 nm), and MEH-PPV (138 nm). The kT/q slope is added as a reference.

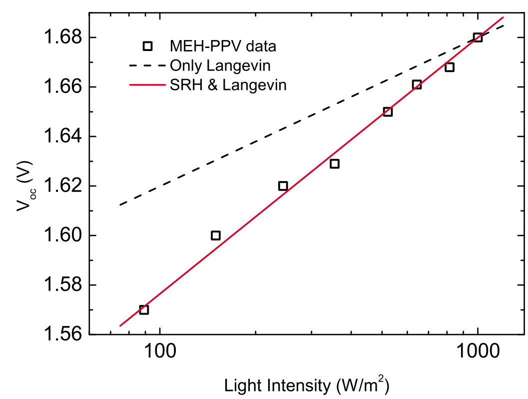

FIG. 2. (Color online) Light intensity dependence of the V_{OC} for MEH-PPV. The experimental data (symbols) is fitted (solid line) using an SRH recombination mechanism in addition to the conventional Langevin recombination (dashed line), which has a slope of kT/q.

$$V_{OC} = \frac{E_{gap}}{q} - \frac{kT}{q}\ln\left(\frac{(1-P)(B_L + B_{\mathrm{SRH}})N_{CV}^2}{PG}\right). \qquad (4)$$

Addition of SRH recombination into the solar cell model then explains the experimentally observed increase in the V_{OC} dependence on light intensity, as shown by Mandoc *et al.*[10,11] The fact that the increase in the V_{OC} dependency on the light intensity indeed originates from traps was further confirmed by deliberately adding traps to the trap free poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene (MDMO:PPV): [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) system.[10] In the present study we investigate the photovoltaic response of standard poly(3,4-ethylenedioxythiophene):poly(4-styrene sulphonic acid)/PPV/Ba/Al PLED structures and specifically examine the dependence of the V_{OC} on the light intensity. All the PPV derivatives used here exhibit a strongly trap-limited electron transport.[2] Modeling of the V_{OC} dependence on light intensity then provides the strength of the trap-assisted recombination. In addition, we explore the consequences of this mechanism on the PLED performance.

A first glance at the light intensity dependence of the V_{OC} for some well-known PPV derivatives (Fig. 1) reveals that for all these materials the slope is considerably higher than kT/q, thus indicating the presence of trap-assisted recombination. For the phenyl-substituted poly[para-phenylenevinylene] copolymer (SY-PPV), poly(2-[4-(3′,7′-dimethyloctyloxyphenyl)]-co-[2-methoxy-5-(3′,7′-dimethyloctyloxy)]-1,4-phenylenevinylene] (NRS-PPV), and poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV), the slopes are 2.1, 1.7, and 1.7 times the thermal voltage, respectively.

Having established that the trap-assisted mechanism is present in these PPVs it is of importance to know how relevant this mechanism is. Since MEH-PPV is the most thoroughly benchmarked[18] and electrically parameterized[2] polymer of this set, this material will be used for further investigation. A numerical device model,[19] in which drift and diffusion of charge carriers, the effect of space-charge on the electric field, density dependent mobility,[20] Langevin type recombination,[15] exponential trap distribution for the electrons,[2] and a field and temperature dependent generation rates of free charge carriers[18] is included, was used to obtain the segmented line in Fig. 2. One can clearly observe that the strength of the free carrier recombination alone, yielding a kT/q slope, is not enough to explain the data correctly. Also for the PLED case we have introduced the SRH mechanism of recombination with trapped electrons according to Eq. (3). Using 9.0×10^{-19} $\mathrm{m^3/s}$ for the electron and hole capture coefficients, the light intensity dependence for the V_{OC} for the MEH-PPV device is perfectly described. This value for the capture coefficient is nearly equal to the value of 1.4×10^{-18} $\mathrm{m^3/s}$ for the case of the polymer:polymer bulk heterojunction solar cell in which also trap-limited electron transport in the acceptor polymer is the limiting factor for the performance of this type of solar cell.[11]

Having determined the strength of the trap-assisted recombination through the V_{OC}-light intensity measurement, it is of interest to find out whether the addition and the strength of this mechanism proves to be significant for the operation of a PLED. Similar to solar cells, in the PLED model the strength of the SRH recombination is added to the Langevin recombination strength resulting in the continuity equations

$$\frac{1}{q}\frac{\partial}{\partial x}J_n = -\frac{1}{q}\frac{\partial}{\partial x}J_p = R = (B_L + B_{\mathrm{SRH}})(np - n_i^2), \qquad (5)$$

where J_n is the electron current, J_p the hole current, and R denotes the recombination rate. As observed in previous studies and again apparent in Fig. 3, for PPV PLEDs Langevin recombination alone is not sufficient to describe the *J-V* characteristics. In order to fit the *J-V* characteristics it was needed to increase the Langevin recombination strength by

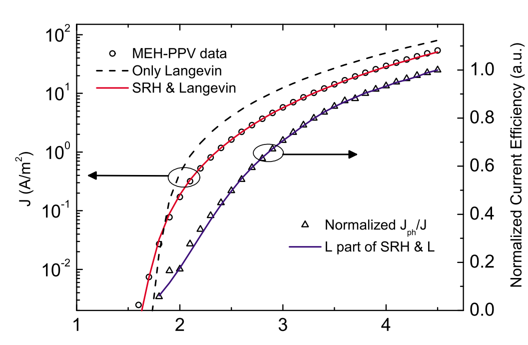

FIG. 3. (Color online) *J-V* characteristics of a 165 nm MEH-PPV PLED and the corresponding fit at 295 K. The dashed line represents the simulation of the current when only Langevin recombination is taken into account. The normalized CE data and fit are plotted to the right axis.

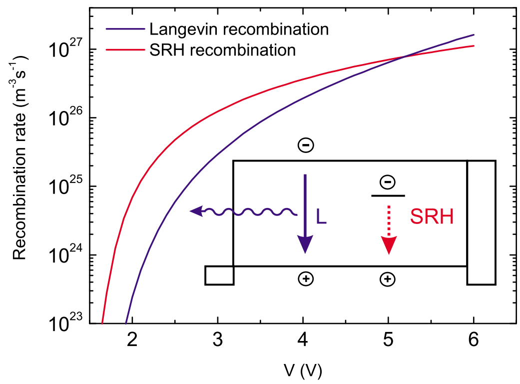

FIG. 4. (Color online) The recombination rate for the two competing recombination processes. The inset depicts a schematic representation of these processes. Only Langevin is assumed to be radiative.

typically a factor 3–4.[8,9] Such a possible deviation has been attributed to filamentary transport, mobility anisotropy and restriction of transport in one dimension.[21] Another proposition for this deviation is a change in the charge carrier mobilities due to the presence of charge carriers of the opposite sign.[22] However, our results, as shown in Fig. 3, demonstrate that the simulation that does include the trap-assisted recombination, using $C_n = C_p = 9.0 \times 10^{-19}$ m^3/s as obtained from the V_{OC} measurements, excellently describes the experimental data, without any correction on the Langevin recombination strength. Moreover, the normalized current efficiency (CE; light output/current) plotted in the same figure on a sensitive double linear scale, taking into account a quenching distance of 8.5 nm from the cathode, is also well described. For the calculation of the CE only free carrier (Langevin) recombination is considered emissive, the trap-assisted recombination is assumed to be nonradiative. The electron traps in MEH-PPV are known to be deeper than 0.4 eV in the bandgap,[23,24] so that radiative recombination of holes with trapped electrons would lead to emission in the near-infrared, which is not observed. Taking into account singlet emission and 20% out-coupling efficiency[25] the external quantum efficiency from the simulation amounts to 1%, which is in good agreement with earlier reports.[8,26]

The SRH and Langevin recombination rates following from the calculations are depicted in Fig. 4. The calculations show that the trap-assisted recombination rate is dominant over the free carrier type at low voltage, however, being surpassed by Langevin recombination at higher electric fields. The different bias dependence originates from the fact that Langevin recombination rate is quadratic in carrier density [$\sim np$], whereas trap-assisted recombination rate exhibits a linear scaling [$\sim n(p)$]. This implies that at low voltages the majority of the recombination that is taking place is recombination of free holes with electrons that occupy a trap site.

In conclusion, through photovoltaic measurements on PPV diodes we have established the presence and the strength of trap-assisted recombination as a complement to the bimolecular Langevin recombination. Including trap-assisted recombination in the PLED device model leads to a consistent *J-V* and efficiency description. The omission of this process rationalizes the previously observed overestimation of the Langevin prefactor. The trap-assisted recombination is a dominant loss mechanism in the PLED at low bias voltage, whereas radiative bimolecular recombination takes over at higher electric fields.

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